Fire safety is crucial to our modern society. Flame retardants play an important role in the fire protection strategy. In recent years, regulatory demands have put enormous pressure on developing environmentally friendly flame retardants for thermoplastics. The aim of this series of articles is to review new flame retardant technology and trends in their use with thermoplastics. It describes advances in non-halogenated flame retardant technologies, new polymeric flame retardant additives, and advances in testing and fire risk evaluation.

Background

Flame retardants are a class of chemicals designed to provide passive fire protection to polymers under specific fire risk scenarios. The fire protection provided by the flame retardant can vary from ignition resistance to slowing of flame spread/heat release growth to smoke and toxic gas reduction. There is a very wide range of actions flame retardants can perform if chosen and implemented properly. It is important to note that every flame retardant solution must be tailored for a specific polymer and for a specific test.

In 2009 the global market for flame retardant chemicals was more than 3 billion pounds, with a value of over $4 billion. This was expected to reach $6.1 billion by 2014. Detailed breakdowns of this market are only available in proprietary marketing reports such as those produced by the Business Communications Company. Important applications include aerospace, automotive, electronics & electrical goods, carpeting, textiles, mass transport (train, ships, subways), building & construction, military, and wire & cable.

A flame retardant will normally be used in a particular product if fire safety engineers anticipate a significant risk of fire exposure that threatens loss of life or property and which cannot be addressed with active fire protection (sprinklers or replacement with non-flammable materials). The amount of flame retardants used in each application will vary depending upon the flammability of the polymer and the severity of the fire risk.

Significant environmental events have captured the public’s attention and led to a general phobia of chemicals in the Western World. These include the Great Smog of London (United Kingdom, 1952), which caused numerous deaths due to emissions and the Cuyahoga River fire (near Cleveland, Ohio, USA, 1969) where the water ‘caught fire’ due to incorrect chemical disposal.
Our society has responded to events like these and made great strides in improving the balance between technological advancement and environmental protection. One result is our ability to detect picogram quantities of pollutants with the help of modern analytical techniques such as gas chromatography – mass spectrometry (GC-MS) and high performance liquid chromatography – mass spectrometry (HPLC-MS). This has shown that flame retardants are widespread in the environment.

Other work has shown that some flame retardants can be persistent, bio-accumulative, and toxic (PBT). This has led to calls for bans on their use and to regulation in the European Union and United States, where the use of some brominated flame retardants is banned.

Plastics containing brominated flame retardants can be difficult to recycle. The first problem is that the flame retardant may migrate out of the plastic as a dust during regrinding. The second one occurs when brominated flame retardant containing plastics are recycled, they can contaminate non-flame retardant plastic waste streams. Finally, in the case that the brominated flame retardant polymer goes to incineration for final disposal, the incinerators must have afterburners and acid capture systems to deal with any dioxin and hydrogen bromide formed. However, some brominated flame retardant containing polymers have shown that they can be reground and remelted into parts many times before losing flame retardant effectiveness. So while there are difficulties in recycling halogen flame retardant containing plastics, it can be done.

Along with chemical phobia and some of the difficulties in dealing with brominated flame retardants at the end of their life cycle, flame retardants seem to have lost in the court of public opinion. For example in May, 2012, a wide-ranging article was published by the Chicago Tribune calling for a ban on an entire chemical class of flame retardants. The perception is that flame retardants serve no purpose. This is based upon a lack of awareness of the balance between the benefits of modern plastics and the fire risks that they bring into the home and workplace.

Flame retardants are a class of chemicals, which are added to combustible materials to provide passive fire protection for specific fire risk scenarios. These additives are designed to minimize the risk of a fire when a plastic comes in contact with a small heat source such as cigarette, candle or an electrical fault. The fire protection provided by the flame retardant can vary from ignition resistance to slowing of flame spread/heat release growth to smoke and toxic gas reduction. Flame retardants can provide this wide range of mechanisms if chosen and used
Flame retardants are examples of polymer additives, which as their name implies, are materials that are added to the plastic at some point during its manufacture, to bring a specific benefit to a plastic (such as improved mechanical, thermal or electrical properties, color, oxygen or UV protection) that the base polymer could not provide on its own.

A wide range of materials are used as flame retardants. There is no such thing as a universal flame retardant, since a material that works well with a polymer in one test may not be appropriate for the same polymer in another test, or for a different polymer in that same test. Every flame retardant application must be tailored for a specific polymer in a specific test. Development of new flame retardant applications requires careful attention to polymer chemistry, polymer thermal decomposition behavior, and the flame retardant mechanism. This is discussed in a number of introductory books and guides.

The most common flame retardants are the brominated flame retardants, which are used due to their great efficacy in a wide range of polymers and applications and their low cost. These materials have been known since the 1930s, and have proved to be effective. However this is an old technology and as we have learnt more about their environmental impact, their risks and benefits have had to be reassessed. At the same time a new class of brominated flame retardants which are polymeric in structure has been appearing in the market place. Their rate of acceptance is being determined by a mix of technical and political factors.

**The Regulatory Situation: Flame Retardant Bans**

The EU has been investigating the PBT issues of this class of chemicals for quite some time. The issue has also been discussed and debated in the US and Canada and over the past 20 years. The greatest change has occurred in the past year; flame retardants that have been in use for decades (such as brominated diphenyl ethers and hexabromocyclododecane (HBCD)) will no longer be allowed after the end of 2013 or 2014. Even with some national regulatory exceptions, the extended use time for these flame retardants is unlikely exceed one or two years.
Current Trends in Flame Retardants for Thermoplastics – Part I
Written by Alexander B. Morgan, Ph.D., University of Dayton Research Institute; Dayton, OH 45469-0170, USA
Monday, 25 February 2013 02:53

In 2006 Pentabromodiphenyl ether and Octabromodiphenyl ether were voluntarily withdrawn by the last major manufacturer of these chemicals (Great Lakes Chemical Corporation, now part of Chemtura) and regulated heavily in the US by the Environmental Protection Agency (EPA), thus ensuring that there would be no new major use of these chemicals.

In 2012, all brominated diphenyl ethers have been voluntarily withdrawn by the main flame retardant manufacturers and also placed under EPA regulatory control for phase-out and banning of import or use in the US. These rules effectively eliminate the use of these flame retardant additives in any new product sold in the US, but this flame retardant may be present in many existing products that already contains that flame retardant. HBCD, used mostly for expanded polystyrene foam insulation, has also been selected for phase out in the USA and Canada.

In one year, two widely used classes of flame retardants have been voluntarily withdrawn by the manufacturers and put under regulatory ban. This has had two major effects, one political, one technical. It has given companies the impetus to develop viable safer commercial alternatives and it has emboldened non-governmental organizations (NGO) to push for further bans.

Current Trends

As indicated in the previous section, the three main manufacturers of brominated flame retardants - Albemarle Corporation, Great Lakes Solutions (Chemtura), and Israel Chemicals Limited - have voluntarily withdrawn HBCD and brominated diphenyl ethers from the market. However, each company also has a variety of replacements for these chemicals. In many cases, the replacement is a polymeric brominated polymer. This is notable in that polymeric materials tend to have a much lower environmental impact (low bio-accumulation and toxicity factors) than small molecules do. This trend of polymeric flame retardants is one that is likely to continue as the flame retardant manufacturers advance this technology. Indeed, polymeric flame retardants may present some superior benefits from a manufacturing perspective, compared to the flame retardants they are replacing. Specifically, they will likely be easier to melt-compound into a plastic, and may give better balance of properties in final plastic products as the final product will be a polymer/polymer blend, not a polymer with fillers/additives present. These polymeric additives, with trade names such as GreenArmor (Albemarle), Emerald Innovation (Great Lakes), and FR122 (Israel Chemicals), are a new trend for 2012 and one that is likely to continue.

Companies outside North America and Europe have no chemical-production bans in their home country, and so continue to manufacture the banned flame retardants, which might continue to appear in imported goods.

The long term future of brominated polymers is not clear. Their commercial viability is threatened by the chemical phobia discussed above, exacerbated by pressure from NGOs, who cast doubt on their value and efficacy while emphasizing perceived health risks associated with the small molecule flame retardants. This is important, as the chemical structures of small molecule brominated flame retardants and brominated polymers may share some similarities (aromatic Carbon-Bromine bonds for example) but a polymer and a small molecule containing the same type of chemical bond will have an entirely different PBT profile. Therefore one should not just assume that all chemical structures have the same environmental and
Every plastic manufacturer must carry out a difficult balancing act when selling a product. The product must meet end-use performance requirements (mechanical, electrical, appearance, thermal, fire, etc.), marketing targets (cost, availability), and customer demands, which can at times be rather fickle. The trend for many consumers of plastics in regards to flame retardants is to go towards non-halogenated technologies. This is due to the perception that halogenated materials (brominated flame retardants, poly(vinyl chloride), etc.) are bad for the environment, whether right or wrong. Therefore customer perception that halogen compounds are always bad may slow the commercialization of new brominated polymers for use in the marketplace. The plastics manufacturer must give the customer what they want or they are not going to make a sale, and very likely we will see continued increases in non-halogenated flame retardant sales and use over the next decade. A significant educational campaign on the part of the flame retardant manufacturers is needed here, and one should expect more discussion on the topic over the next several years. This discussion carries into the next topic, the effects of politics on fire vs. environmental safety.

The Situation: Fire Safety vs. Environmental Safety

With the Chicago Tribune article and two successful bans of flame retardants, some groups are now turning their focus promoting bans on the use of flame retardants in many applications. If the chemical cannot be banned, then these organizations fight to prevent their use in specific applications, whether or not this position is supported by scientific data. An example is provided by efforts to revise the fire safety standards for upholstered furniture in the US, starting with a revision of California Technical Bulletin 117 (TB-117), which governs the response of polyurethane foam to small open flames.

In this author’s opinion, not all flame retardants should be used at all costs. If there is good data showing that the fire protection benefits from a flame retardant are outweighed by environmental damage, then that flame retardant should not be used. If there is good scientific data showing that there is a satisfactory replacement for the old flame retardant which provides good fire safety performance and lowered environmental impact, then the old flame retardant should be removed and the replacement inserted. The wrong approach would be to ban flame retardants with no consideration of fire safety. For the TB-117 revision, the push is to focus on removing the small open flame ignition source and instead use a smoldering cigarette ignition source. However, since cigarettes in the US are mostly self-extinguishing (with the exception of hand-rolled cigarettes) the standard revision seems to be focusing on what could be a less common fire risk; ignition by cigarettes. TB-117 began long ago as a way to provide fire safety against cigarette ignition by testing with a fire source worse than a smoldering cigarette. If the argument is that the fire risk scenario has changed, then it’s time to look at both the regulatory standard and the fire risk. If cigarette ignition is not really the hazard, but the heat release of
polyurethane foam can cause major fire losses, then one should focus on instead on overall material flammability tests, like heat release requirements via calorimetric measurements. The furniture industry does not need to be literally and figuratively burned again by fire standards that open them up to liability suits. Similarly, the path away from the lawsuits will not be met by abandoning flame retardants. The fire risks associated with polyurethane foams are quite obvious, but so far in the discussion these fire risks seem to be ignored.

Both the flame retardant manufacturers and organizations opposing them have used political hearings promote their positions. One side promotes their products as enhancing fire safety while the other argues that the chemicals are all hazardous and do not provide any meaningful benefit. The truth of the matter is that both are partly right, and they should be working together to come up with better solutions. In some cases, the polyaromatic hydrocarbons and dioxins released from a large house fire, initiated by a non-flame-retarded product, can generate far more environmental pollution than the release of flame retardant into the environment when no accidental fire occurred. In modern homes, with many synthetic polymers present, once fires are started, they grow faster and burn hotter/quicker than fires of old, thus leading to more large fires with significant emissions. This is demonstrated in a recent video of a fire study conducted by Underwriter’s Laboratories and the US National Institute of Standards and Technology shows that a room with modern furnishings can burn much faster than one filled with older materials.

Conclusions

Fire risk will always be with us, and so the question needs to be asked what level of risk are we willing to live with? Should we accept a higher chance of loss of property and life in fires in order to reduce environmental and health damage? As a scientist one would argue that we should be asking for and demanding a reduced fire risk without environmental harm. Just as we have made great strides in detecting chemicals through research and innovations in analytical techniques, we have made similar strides in developing new chemicals in which adherence to green chemistry methods and environmental impact are considered. Assuming that all participants can agree that both fire safety and the environment are important, a rational scientific approach can be developed that considers environmental toxicity and life cycle analysis in the development of new flame retardant materials. Such collaboration would be incredibly fruitful for our society, and it is sorely needed.

References


Alexander B. Morgan, Ph.D.

After receiving a B.Sc from the Virginia Military Institute (1994) and a Ph.D. from the University of South Carolina (1998), Dr. Morgan has worked for over seventeen years in the areas of materials flammability, polymeric material flame retardancy, fire science, fire testing, and fire safety engineering with an emphasis on chemical structure property relationships and fire safe material design. His current research areas include New Flame Retardant Technology for Polyurethane Foam and Furniture, New Flame Retardant Technology with Reduced Environmental Impact, Fire Testing Method Development, Waste-To-Energy Pyrolysis and Combustion Science and Thermal Degradation and Stability Behavior of Materials.

Dr. Morgan has helped academic, government, and industrial customers solve their flame retardant and fire safety needs in a wide range of applications. He is on the editorial review
boards for two fire safety journals (Fire and Materials, Journal of Fire Science), and is a member of ASTM, Sigma Xi, International Association of Fire Safety Scientists, and the American Chemical Society.